

# ANALYSIS OF ORGANIC / INORGANIC ANALYTES IN ENVIRONMENTAL SAMPLES BY PACKED CAPILLARY CHROMATOGRAPHY

Mark D. Burford<sup>1</sup>, Neil G. Smart<sup>2</sup>, Mark M. Robson<sup>1</sup>, Stuart C. Mitchell<sup>1</sup>,  
Keith D. Bartle<sup>1</sup> and Antony A. Clifford<sup>1</sup>

<sup>1</sup> School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

<sup>2</sup> British Nuclear Fuels plc, Springfield Works, Salwick, Preston PR4 0XJ, UK.

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## INTRODUCTION

Recent progress in the development of techniques for packing of high efficiency capillary columns has enabled the concept of unified chromatography to be realised [1]. Packed capillary columns offer the advantages of both packed column (high loading capacity, wide range of stationary phases) and capillary column (speed of analysis, high resolution) techniques to produce a versatile and efficient analytical procedure. For the detailed investigation of fossil fuel and environmental samples the rapid growth of packed capillary chromatography offers the unique opportunity to analyse both organic and inorganic components as the column can be operated in both gas chromatography (GC) and supercritical fluid chromatography (SFC) modes. In this study, the use of packing capillary columns, prepared in-house, is investigated for both high pressure GC and SFC using helium and CO<sub>2</sub> as the mobile phase respectively. Several spiked and real world samples have been used to demonstrate the potential of packed capillary columns in the analysis of organic and inorganic analytes in fuel and environmental samples.

## EXPERIMENTAL

### *Column packing procedure*

A number of fused silica capillary columns, of varying length, were packed using supercritical CO<sub>2</sub> at 300 bar. The fused silica tubing was connected to a packing reservoir, cleaned with methanol and dried. The packing material was then placed in the reservoir. The end of the reservoir was connected to a high pressure valve which facilitated the introduction of the mobile phase. The end of the column was connected, via a Valco union containing a metal screen (2 µm), to a linear restrictor (12 µm i.d. x 30 cm fused silica tubing). The column tubing and restrictor were then immersed in an ultrasonic bath (-60-70°C). Liquid CO<sub>2</sub> was introduced into the system by opening both valves. The column was continuously sonicated at constant pressure throughout the packing procedure. On completion, sonication was stopped whilst the pressure was maintained for a further 30 minutes approximately, prior to depressurisation. The depressurisation step was performed slowly to avoid backflushing and possible deformation of the packed bed. At a pressure of 70-80 bar, both valves were closed and the system vented. The column was then ready for use.

### *High pressure gas chromatography*

Two different packed capillary stationary phases were evaluated for the analysis of light hydrocarbons. The fused silica columns, i.d. of 250 µm, were packed with either 5 µm ODSII (C<sub>18</sub>) or 5 µm hexyl (C<sub>6</sub>) (Phase Separations, Deeside, UK). Three different column lengths (10, 20 and 30 cm) were installed in a Lee Scientific 600 Series SFC oven fitted with a Valco AC14LTWP injection valve and an FID. All samples were injected neat by varying the injection time. The system was evaluated using high pressure helium (20-100 bar) and carbon dioxide (40-65 bar).

### *Supercritical fluid chromatography (SFC)*

The chromatographic system comprised an RPT 9400 (RPT Inc., San Jose, California) micro SFC pump, Lee Scientific 600 Series SFC oven, Lee Scientific micro UV detector and a Merck-Hitachi D2500 integrator. A valco AC14LTWP injection valve with an injection volume of 200 nl was used. The various components were connected via silica capillary. A 12 µm linear restrictor was located after the UV-VIS detector and heated to 350°C to avoid blockages. The system was operated manually.

## RESULTS AND DISCUSSION

### *High pressure gas chromatography*

Microcolumns packed with conventional gas GC packings have previously been investigated at high pressures by Giddings and coworkers [2]. However, only recently has the use of LC packings been explored in high pressure packed capillary GC by Liu and Yang [3]. Conventional packing techniques introduce the stationary phase as a slurry but a new packing technique using supercritical CO<sub>2</sub> have been shown to provide a significant improvement in packing and column efficiency [1]. In the present study, to evaluate column performance helium

was used as the mobile phase in the analysis of low molecular weight hydrocarbons. Figure 1 shows the chromatogram obtained from the analysis of a 12 component synthetic mixture of  $C_3$ - $C_8$  hydrocarbons using a 20 cm x 250  $\mu$ m i.d. column packed with 5  $\mu$ m octadecylsilica (ODS- $C_{18}$ ). At 120 bar helium pressure, complete separation of all 12 compounds was achieved within 20 minutes. The resolution obtained from the analysis of the mixture containing six  $C_6$  isomers and four  $C_8$  isomers demonstrates the high efficiency provided by high pressure packed capillary GC for the separation of light hydrocarbon geometrical isomers. The separation is comparable to that achieved using open tubular capillary columns but with a considerably reduced analysis time. Furthermore, due to the higher sample loading of the packed column, it is possible to inject the sample directly thus avoiding any possible discrimination effects normally associated with split-splitless injection when using open tubular capillary columns. The full range of the ODS column with helium as the mobile phase is shown in Figure 2 for the analysis of a light naphtha standard (Supelco 4-8265) conducted under the same conditions as above. From the chromatogram it is clear that the low molecular weight compounds are well-resolved but as the molecular weight increases the resolution tails off indicating the current limit of the technique. Analysis of the standard by an open tubular chromatography confirmed this observation, with separation of the higher molecular weight compounds reduced considerably. However, the overall analysis time was also reduced by approximately one third.

#### *Supercritical fluid chromatography (SFC)*

The chromatographic analysis of the organic and metallic components recovered from fuel and oil related environmental samples generally involves two specific separation techniques due to the distinctive chemical and physical characteristics of both types of analytes. The organic components of interest such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and petroleum hydrocarbons are sufficiently volatile to be amenable to capillary gas chromatography (GC). However, the organometallic and inorganic species, which in general cannot be volatilized or are thermally unstable at GC operating temperatures are chromatographically separated using ion-exchange or high performance liquid chromatography (HPLC) [4].

The use of supercritical fluid chromatography (SFC) has proved to be a suitable technique for the analysis of a wide range of organic compounds. For example, the separation and identification of the EPA priority PAHs in a coal tar oil can be achieved using a 30 cm x 250  $\mu$ m i.d. capillary column packed with 5  $\mu$ m ODS1 stationary phase (See Figure 3). The use of this short column which contained a tailor made PAH stationary phase (Phase Separations, Deeside, UK) eluted the 16 priority PAHs within 30 minutes. Whilst the elution of organic components by supercritical fluids is readily attainable, the elution of metal ions is considerably more difficult due to the charge neutralisation required to solvate ions in the mobile phase [5]. Furthermore, previous studies have demonstrated that ionic organometallic compounds result in poor peak shapes due to their chemical reactivity with the stationary phase [6]. However, by chelating the metal ion with a ligand to form a neutral metal complex the solubility and hence the chromatography of the metal species can be significantly improved [7].

Initial SFC investigations of common metal complexes such as metal dialkylthiocarbamates (DDC) used packed columns with an organically modified carbon dioxide ( $CO_2$ /MeOH) mobile phase. More recently, capillary GC with pure carbon dioxide has offered improved resolution [8], but the technique requires that the metal DDC complex be sufficiently soluble in the mobile phase to avoid broad peak shapes and poor reproducibility [7]. Packed capillary chromatography offers the advantages of both a packed column (e.g. high loading capacity and a wide range of stationary phases) and a capillary column (e.g., speed of analysis and high resolution) and therefore metal DDC complexes with relatively low solubility can be adequately resolved using just pure  $CO_2$ . Figure 4 shows the chromatogram of an organic extract containing the DDC ligand and the metal complexes  $Fe(DDC)_3$  (7  $\mu$ g) and  $Ni(DDC)_2$  (14  $\mu$ g).

Organometallic compounds can also be separated using the same 20 cm packed capillary ODS1 column (Figure 5) with pressure programming. Both ionic (triphenyltin chloride) and non-ionic (tetraphenyltin, triphenylarsenic and ferrocene) species were detected with good chromatographic peak shapes. Earlier studies have found that the presence of an anionic functional group increases the polarity and chemical reactivity of the organometallic compounds, which consequently results in poor peak shapes [6] and/or incomplete recovery of injected samples [9]. Thus the elution of the ionic components has previously required an organic modifier to avoid peak tailing [6], however this addition step was not necessary with the packed capillary system.

The wide range of metal complexes and organometallic species that are amenable to SFC should also be amenable to supercritical fluid extraction (SFE), and several researchers have adequately demonstrated this application [5,10]. For example, the diethyldithiocarbamate (DDC) metal complexes analysed by packed capillary are generally poorly soluble in low pressure (150 atm) and low temperature (50°) carbon dioxide [5], with solubility values in the region of  $10^{-7}$  -  $10^{-6}$  mol/L. Consequently, the complexes are difficult to elute from the packed capillary column without high pressures (350 atm) (See Figure 5). Thus, if the temperature and pressure of the supercritical fluid is substantially increased the solubility of the metal DDC complexes will also increase, as shown in Table 1.

Table 1. Solubility of cadmium (II) diethyldithiocarbamate in CO<sub>2</sub>.

CO <sub>2</sub> conditions	Solubility (mol/L)
250 atm, 50°C	$3.6 \times 10^{-6}$
250 atm, 100°C	$1.6 \times 10^{-5}$
350 atm, 50°C	$5.3 \times 10^{-6}$
350 atm, 100°C	$6.5 \times 10^{-5}$

Using high pressure carbon dioxide (400 atm) to solvate the DDC ligand it was possible to recover between 50 and 70% of spiked Pb<sup>2+</sup> and Cd<sup>2+</sup> from filter paper. It is envisaged that further extractions of the metal ions with fresh complexing agent at this rigorous extraction condition could potentially achieve quantitative SFE recoveries.

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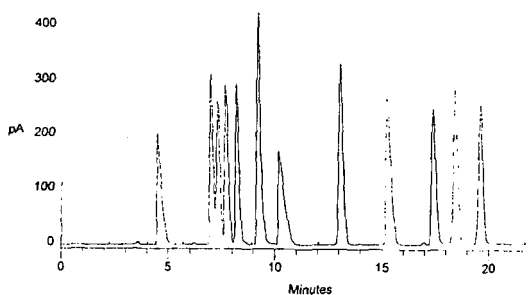


Figure 1  
High pressure gas chromatogram of a mixture of: 1 Pentene, 2 Methyl Pentene, 3 Methyl Pentene, 2 Methyl Pentene, 2, 3 Dimethyl Butane, Methyl Cyclopentane, Cyclohexane, 3 Methyl Hexane, 3 Methyl Heptane, Octane, 2, 2, 4 Trimethyl Pentane, 2, 2, 4 Trimethyl Pentane.  
Conditions: 20 cm, 250  $\mu$ m ID, octadecylsilica column (Phase-Separations, Deeside, UK), Helium mobile phase at 120 bar, with the following temperature program: 4 minutes isothermal at 40°C, 50°C per minute ramp to 220°C

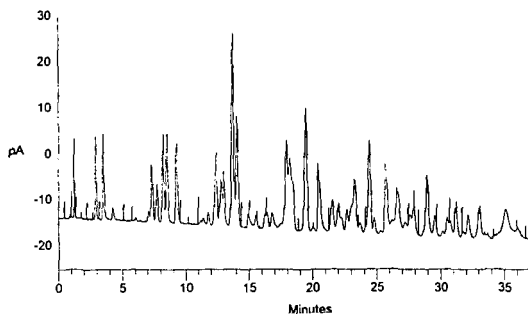


Figure 2  
High pressure gas chromatogram of a light naphtha standard (Supelco 4-8265)  
Conditions: 20 cm, 250  $\mu$ m ID, octadecylsilica column (Phase-Separations, Deeside, UK), Helium mobile phase at 120 bar, with the following temperature program: 4 minutes isothermal at 40°C, 50°C per minute ramp to 220°C

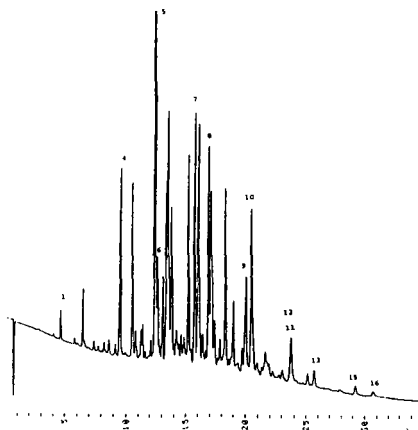


Figure 3  
Supercritical fluid chromatogram of base coal tar oil analysed using the following conditions:

Column: PAH 5  $\mu\text{m}$  (Phase-Separations, Deeside, UK), 30 cm column, 250  $\mu\text{m}$  I.D. column oven temperature 100°C, detector wavelength 254, with the following gradient: 100 to 300 bar  $\text{CO}_2$  and 0.10 to 1.00  $\mu\text{L}/\text{min}$  methanol over 30 minutes. Peak identification; 1 naphthalene; 2 acenaphthene; 3 acenaphthylene; 4 fluorene; 5 phenanthrene; 6 anthracene; 7 fluoranthene; 8 pyrene; 9 benzo[a]anthracene; 10 chrysene; 11 benzo[b]fluoranthene; 12 benzo[k]fluoranthene; 13 benzo[a]pyrene; 14 dibenzo[a,h]anthracene; 15 benzo[ghi]perylene; 16 indeno[1,2,3-cd]pyrene.

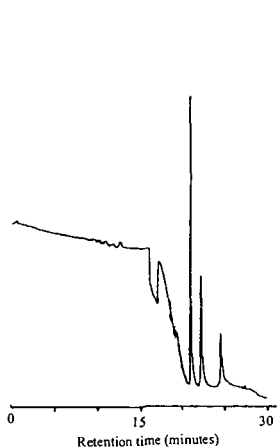


Figure 4. SFC separation of a mixture of DDC,  $\text{Fe}(\text{DDC})_3$  and  $\text{Ni}(\text{DDC})_2$  using a 20 cm x 250  $\mu\text{m}$  I.D. capillary column packed with 5  $\mu\text{m}$  ODS1 stationary phase. Separation obtained with carbon dioxide pressure programme starting at 100 atm and increasing the pressure at 16 atm/min to 350 atm, then holding the pressure at 350 atm for 15 minutes. UV detection at 220 nm.

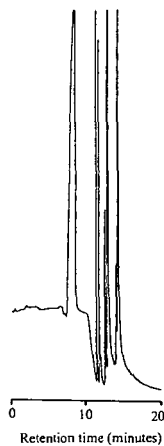


Figure 5. SFC separation of organotin, organoarsenic and ferrocene compounds using a 20 cm x 250  $\mu\text{m}$  I.D. capillary column packed with 5  $\mu\text{m}$  PAH stationary phase. Separation obtained with carbon dioxide pressure programme starting at 100 atm and increasing the pressure at 16 atm/min to 350 atm, then holding the pressure at 350 atm for 15 minutes. UV detection at 220 nm.